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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] In detail this invention about the photosensitive resin composition containing alkalis soluble resin and it to the photosensitive resin composition and can which can form micro pattern structure especially, As a positive resist for creating the mask for circuit manufacture of the thin film transistor (TFT) circuit for integrated circuit (IC) liquid crystal displays (LCD), etc., It is related with the still more suitable positive type photosensitive resin composition also as permanent film formation materials, such as micro lenses, such as interlayer insulation films, such as a liquid crystal display element, an integrated circuit device, and a solid state image pickup device, and a solid state image pickup device.

[0002]

[Description of the Prior Art] Generally, in manufacture of electronic parts, such as a liquid crystal display element, an integrated circuit device, and a solid state image pickup device, the insulator layer for maintaining the flattening film for carrying out flattening of the protective film for preventing the degradation and damage and the element surface and electric insulation, etc. are provided. In the thin film transistor (it is hereafter described as "TFT".) mold liquid crystal display element, or the integrated circuit device, in order to insulate between the wiring arranged in layers, the interlayer insulation film is used. Generally, in manufacture of electronic parts, such as TFT for LCD, and IC, while having the high resolution below a submicron, the resist which has high sensitivity is demanded strongly.

[0003]For example, the chemical resistance which is not invaded by adhesion or an etching reagent with a substrate is needed for the resist pattern formed by the wet etching method of IC silicon wafer. When an ion yne plastic process is added, the heat resistance which can bear heating at high temperature is required. Transparency is also required in order to use as an insulating material of TFT furthermore. However, in order to discolor by heat-treating, there is a

fault that it cannot be used for optical materials, such as a protective film of a liquid crystal color filter and a micro lens.

[0004]Interlayer insulation film formation has many required routing counters, and is difficult to secure the various characteristics required of an interlayer insulation film, i.e., surface smoothness, high resolution nature, development nature, heat resistance, chemical resistance, adhesion with a substrate, transparency, insulation, etc. good, and there was no photosensitive resin composition with which it is satisfied of all of these various characteristics. In order to control generating of a cross talk in connection with the densification of a device about an interlayer insulation film, the low dielectric was demanded, but it was not satisfactory enough at the point of reconciling these various characteristics and a low dielectric in the conventional photosensitive resin composition.

[0005]Although the radiation-sensitive resin composition which consists of a 4-(4-hydroxyphenyl) cyclohexanone phenol system compound and alkalis soluble resin is indicated by JP,6-242599,A and JP,6-321890,A, In the pattern formation characteristics, such as heat resistance, it was not satisfactory enough.

[0006]On the other hand, in order to improve the various characteristics of a photosensitive resin composition or a radiation-sensitive resin composition, much proposals are made about the constituent containing alkalis soluble resin or it until now. For example, the alkali solubility polymer which becomes JP,6-18702,A from the copolymer of hydroxystyrene and styrene, The photosensitive resin composition for lenses containing the compound which has at least two epoxy groups in 1,2-naphthoquinonediazide sulfonic ester and intramolecular is indicated. In JP,6-136239,A, alkalis soluble resin, 1, 2-naphthoquinonediazide compound, The radiation-sensitive resin composition for micro lenses containing the compound, the melamine and trihalomethyl triazine, or onium salt which contains two or more epoxy groups in intramolecular is indicated. The radiation-sensitive resin composition containing alkali solubility cyclic polyolefin system resin, 1, and 2-naphthoquinonediazide compound and a cross linking agent is indicated by JP,10-307388,A. The alkalis soluble resin which becomes JP,11-52560,A from a copolymer with unsaturated carboxylic acid, an epoxy group content radical polymerization nature compound, and other olefin system unsaturated compounds, The radiation-sensitive resin composition containing a 1,2-naphthoquinonediazide compound and a nitrogen content cross linking agent is indicated. The radiation-sensitive resin composition for micro lenses containing a copolymer with unsaturated carboxylic acid, epoxy group content (meta) acrylate, and other olefin system unsaturated compounds and 1 and 2-naphthoquinonediazide compound is indicated by JP,2000-327877,A.

[0007]However, in the conventional resin composition, the constituent it is satisfied with the various characteristics required of a positive type photosensitive resin composition, i.e., high sensitivity, of the constituent in surface smoothness, high resolution nature, development

nature, heat resistance, chemical resistance, adhesion with a substrate, transparency, insulation, etc. was not obtained.

[0008]

[Problem(s) to be Solved by the Invention] Can develop the purpose of this invention with an alkaline aqueous solution, are high sensitivity, and moreover, Surface smoothness, high resolution nature, development nature, heat resistance, solvent resistance, adhesion with a substrate, transparency, the photosensitive resin composition containing the alkalis soluble resin which can form easily the pattern state thin film which was excellent in various characteristics, such as insulation, -- further, There is realizing simultaneously with the above-mentioned various characteristics conventionally in providing the photosensitive resin composition which can form easily the pattern state thin film which was excellent in the difficult low dielectric property.

[0009]

[Means for Solving the Problem] According to this invention, a photosensitive resin composition of the following composition is provided and the purpose of describing this invention above is attained.

[0010](1) at least -- N-(4-hydroxyphenyl) maleimide -- 50-mol % -- alkalis soluble resin which consists of a copolymer to contain, 1, 2-naphthoquinonediazide group content compound, and a positive type photosensitive resin composition containing a cross linking agent at least.

[0011](2) A positive type photosensitive resin composition given in the above (1), wherein 1 and 2-naphthoquinonediazide group content compound is a cyclohexane derivative.

[0012](3) A positive type photosensitive resin composition the above (1), wherein a cross linking agent is a melamine compound, or given in (2).

[0013](4) A positive type photosensitive resin composition given in any 1 paragraph of above-mentioned (1) - (3), wherein a cross linking agent is epoxy compound.

[0014]

[Embodiment of the Invention] Hereafter, the photosensitive resin composition of this invention is explained in full detail. Each ingredient first blended with the photosensitive resin composition of this this invention is explained.

[I]at least -- N-(4-hydroxyphenyl) maleimide -- 50-mol % -- the alkalis soluble resin (henceforth "resin (A)") which consists of a copolymer to contain

[0015]resin (A) of this invention -- at least -- N-(4-hydroxyphenyl) maleimide -- 50-mol % -- desirable -- more than 60 mol % -- more -- desirable -- more than 65 mol % -- what is necessary is just resin to contain, and other copolymer components may be contained as a constitutional unit. Although other copolymer components in particular are not limited, as other desirable copolymer components, (1) styrene monomer, (2) (meta) acrylic ester, (3) (meta) acrylic-acid-series monomer, unsaturated carboxylic acid besides (4), etc. are mentioned.

Other copolymer components are independent, or may be combined two or more sorts and may be used. Especially as other copolymer components, (1) styrene monomer and/or (2) (meta) acrylic ester are preferred, and 2 yuan or the 3 yuan copolymer to which copolymerization of these was carried out is preferred especially as resin (A) of this invention.

[0016](1) At least by alpha-, o-, m-, or p-, a styrene monomer is styrene which may be replaced and as the substituent, An alkyl group (preferably carbon numbers 1-4), an alkoxy group (preferably carbon numbers 1-4), halogen (fluoride, chlorine, bromine, iodine), a halo alkyl group (the alkyls in a halo alkyl group are the carbon numbers 1-3 preferably), a nitro group, a cyano group, an amide group, a hydroxy group, etc. are mentioned. Specifically, styrene, alpha-methylstyrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, p-vinyltoluene, p-methoxy styrene, o-, m-, or p-hydroxystyrene etc. are mentioned. Especially a desirable styrene monomer is styrene.

[0017](2) (meta) Ester of acrylic ester may be any of non-annular (straight chain shape or branched state) alkyl ester, alicyclic alkyl ester, aryl ester, and alkenyl ester. The desirable carbon numbers of un-annular alkyl ester are 1-5, the desirable carbon numbers of alicyclic alkyl ester are 3-15, the desirable carbon numbers of aryl ester are 6-16, and the desirable carbon numbers of alkenyl ester are 2-4. Specifically as acrylic acid (meta) un-annular alkyl ester, For example, methyl (meta) acrylate, ethyl (meta) acrylate, n-propyl (meta) acrylate, i-propyl (meta) acrylate, n-butyl (meta) acrylate, sec-butyl (meta) acrylate, tert-butyl (meta) acrylate, pentyl (meta) acrylate, neopentyl (meta) acrylate, isoamyl hexyl (meta) acrylate, propargyl (meta) acrylate, glycidyl (meta) acrylate, etc. are mentioned. (Meta) As acrylic acid alicyclic alkyl ester, Cyclohexyl (meta) acrylate, adamantyl (meta) acrylate, Dicyclopentanil (metha)acrylate, 2-methylcyclohexyl (meta) acrylate, dicyclopentanil oxyethyl (meta) acrylate, isoboronyl (meta) acrylate, furil (meta) acrylate, furfuryl (meta) acrylate, etc. are mentioned. (Meta) As acrylic acid aryl ester, Phenyl (meta) acrylate, triphenylmethyl (meta) acrylate, Naphthyl (meta) acrylate, anthracenyl (meta) acrylate, Anthraquinonyl (meta) acrylate, piperonyl (meta) acrylate, Sall Chill (meta) acrylate, benzyl (meta) acrylate, FENESHIRU (meta) acrylate, KURESHIRU (meta) acrylate, cumyl (meta) acrylate, etc. are mentioned. (Meta) As acrylic acid alkenyl ester, vinyl (meta) acrylate, allyl (meta) acrylate, butenyl (meta) acrylate, etc. are mentioned.

[0018]These ester may have a substituent and a hydroxy group, halogen, an amino group, a nitro group, a cyano group, an amide group, etc. are mentioned as a substituent. In this invention, methyl (meta) acrylate, t-butyl (meta) acrylate, and ethyl (meta) acrylate are preferred especially as acrylic ester (meta).

[0019](3) (meta) as an acrylic acid series monomer, Acrylic acid, methacrylic acid, and these alpha positions A halo alkyl group (the alkyls in a halo alkyl group are the carbon numbers 1-3 preferably), The substitution product replaced by an alkoxy group (preferably carbon numbers

1-3), halogen (fluoride, chlorine, bromine, iodine), the nitro group, and the cyano group is mentioned.

[0020](4) As other unsaturated carboxylic acid, maleic acid, a maleic anhydride, fumaric acid, anhydrous fumaric acid, citraconic acid, mesaconic acid, itaconic acid, 1,4-cyclohexene dicarboxylic acid, etc. are mentioned.

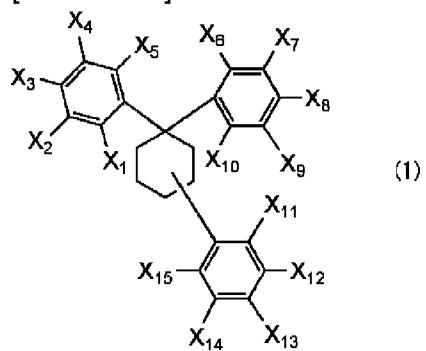
[0021]As a copolymer component of others other than the desirable copolymer component of above-mentioned (1) - (4), Vinylhydroquinone, 5-vinylpyrogallol, 6-vinylpyrogallol, Polyhydroxy vinyl phenols, such as 1-vinylfluoroglycinol; o-, m-, p-vinylbenzoic acid or such alkyls, alkoxy ** halogen, Nitro, cyano, amide, an ester interchange object; Methyl of the unsaturated carboxylic acid of the bivalence of the above (4), Ethyl, propyl, i-propyl, n-butyl, sec-butyl, ter-butyl, Phenyl, o-, m-, p-tolyl half ester, or half amide; Butadiene, Olefins, such as isoprene and a neoprene; The anilide of methacrylic acid or acrylic acid, Amide or N,N-dimethyl, N,N-diethyl, N,N-dipropyl, N,N-diisopropyl, anthranilamide, acrylonitrile, An acrolein, a methacrylonitrile, VCM/PVC, a vinylidene chloride, vinyl fluoride, fluoridation vinylidene, N-vinyl pyrrolidone, vinylpyridine, vinyl acetate, N phenylmaleimide, an N-methacryloyl phthalimide, N-acryloyl phthalimide, etc. may be used together. In this invention, the thing of average molecular weight of 1,000-100,000 is preferred, and this resin (A) is 3,000-70,000 more preferably. When average molecular weight is too low, it is deficient in film formation ability, ***** becomes intense at the time of development, and on the other hand, when too high, developing time may turn into a long time and may have an adverse effect on a substrate.

[0022]The loadings of this resin (A) in the photosensitive resin composition of this invention are 45 - 85 mass part preferably [blending in the range of 35 - 95 weight section] among resin (A), 1, 2-naphthoquinonediazide group content compound, and the total 100 mass part of a cross linking agent, and more preferably. Since transparency, insulation, and coat nature will fall if loadings are too low, sensitivity will fall on the other hand if there are too many loadings, and curing failure is caused, it is not desirable. The photosensitive resin composition of this invention can use other alkalis soluble resin together with the above-mentioned alkalis soluble resin (A). This resin that can be used together is described also as resin (a). The alkali solubility cyclic polyolefin system resin indicated to JP,10-307388,A as resin (a), The unsaturated carboxylic acid indicated to JP,2000-327877,A, Epoxy group content (meta) acrylate and a copolymer with other olefin system unsaturated compounds, The copolymer of acrylic resin and styrene which have the polymerization nature group indicated to the application for patent 2001-158981, and acrylic acid (meta), the copolymer of benzyl (meta) acrylate and acrylic acid (meta), etc. are mentioned. As for resin (a) in which these concomitant use is possible, it is preferred that the ranges of acid value are 30-180. a molecular weight -- 1,000-100,000 -- it is 3,000-70,000 more preferably. 0-30 mass % resin (a) receives resin (A) -- usually -- 0 - 50 mass % -- it is used preferably.

[0023][II]1, 2 - 1, 2 which are used for the constituent of naphthoquinonediazide group content compound this invention - 1, 2 as shown, for example with a following general formula (1) as a naphthoquinonediazide group content compound - The cyclohexane derivative containing a naphthoquinonediazide group is mentioned.

[0024]

[Formula 1]



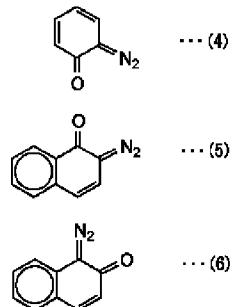
[0025]Although X_1 - X_{15} may be the same, or it may differ and the basis (D is an organic group which has a hydrogen atom or a quinone diazide skeleton here.) shown by the hydrogen atom, the alkyl group, an alkoxy group, or -OD is shown in a general formula (1), However, at least one of X_1 - the X_{15} is -OD group. And 2-5 pieces are organic groups which have a quinone diazide skeleton still more preferably 1-5 pieces preferably at least one in two or more D [a general formula (1)]. As for at least one of at least one and X_6 of X_1 - X_5 - the X_{10} , in a general formula (1), it is preferred that it is -OD group.

[0026]In X_1 - X_{15} , as an alkyl group, a thing of the carbon numbers 1-4 is preferred, and can mention a methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl group, t-butyl group, etc. as the example. As an alkoxy group, a thing of the carbon numbers 1-4 is preferred, and can mention a methoxy group, an ethoxy basis, n-propoxy group, n-butoxy group, etc. as the example.

[0027]- A quinone diazide skeleton in D of OD group is a skeleton preferably expressed with a following general formula (4), a following general formula (5), or a general formula (6).

[0028]

[Formula 2]



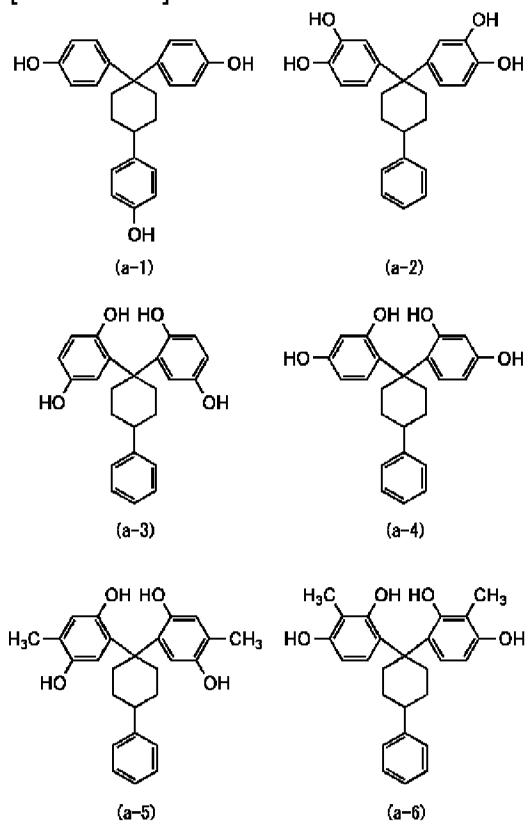
[0029] As an organic group which has such a quinone diazide skeleton, For example, a 1,2-benzoquinone diazido 4-sulfonyl group, 1, a 2-naphthoquinonediazide 4-sulfonyl group, A 1, 2-naphthoquinonediazide 5-sulfonyl group, 1, 2-quinone diazide 6-sulfonyl group, 2, 1-naphthoquinonediazide 4-sulfonyl group, 2, and 1-naphthoquinonediazide 5-sulfonyl group etc. are shown. Before long, a 1 and 2-naphthoquinonediazide 4-sulfonyl group and 1, and 2-naphthoquinonediazide 5-sulfonyl group is especially preferred.

[0030] In a general formula (1), a compound which corresponds when a compound which corresponds when all D is hydrogen atoms, i.e., a basis shown by aforementioned -OD, is a hydroxyl group is a precursor of a compound expressed with a general formula (1) [a precursor of a general formula (1) is hereafter called "compound (a)"].

[0031] As an example of compound " (a)", a compound expressed with following formula (a-1) - (a-18) can be mentioned.

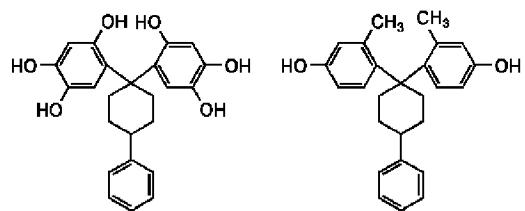
[0032]

[Formula 3]

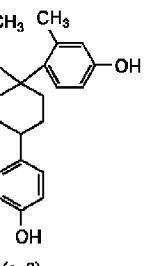


[0033]

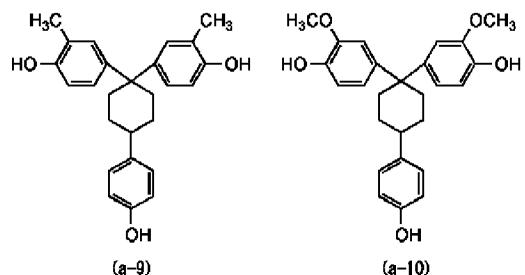
[Formula 4]



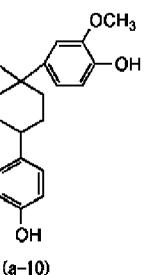
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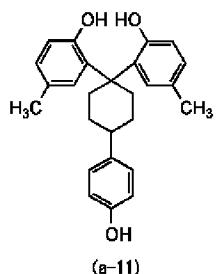
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(a-9)



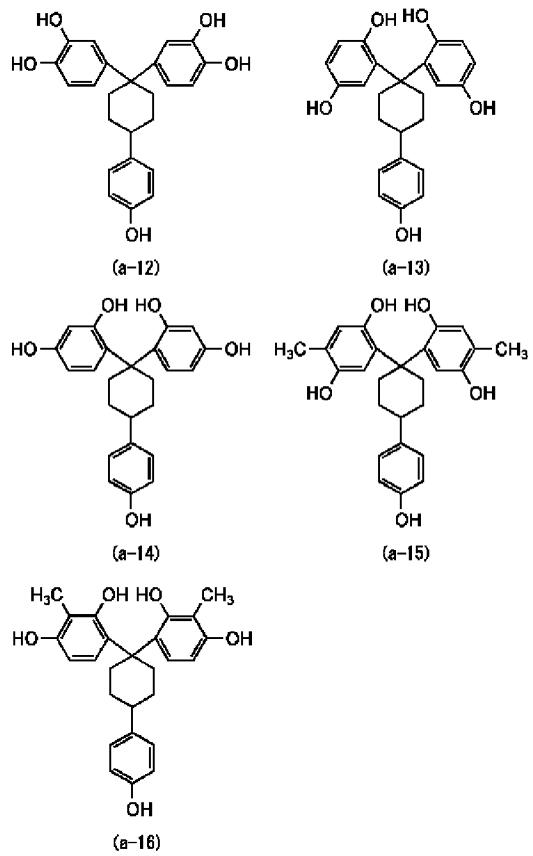
(a-10)



(a-11)

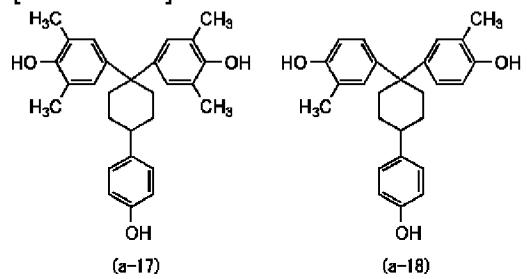
[0034]

[Formula 5]



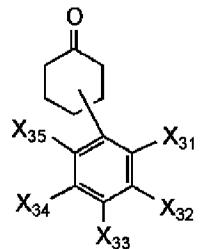
[0035]

[Formula 6]



[0036]The ketone compound by which the above-mentioned compound (a) is expressed with phenols and a following general formula, for example [0037]

[Formula 7]



[0038]X₃₁ - X₃₅ are the same or different among a formula -- a hydrogen atom. an alkyl group

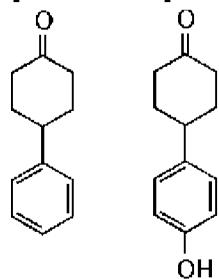
-- desirable -- the alkyl group of the carbon numbers 1-4, and an alkoxy group -- the alkoxy group or hydroxyl group of the carbon numbers 1-4 is shown preferably. It can manufacture by making it react under existence of an acid catalyst.

[0039]As these phenols, phenol, o-cresol, m-cresol, P-cresol, a 2,5-xylenol, a 3,4-xylenol, resorcinol, Catechol, hydroquinone, methylhydroquinone, a phloroglucinol, pyrogallol, p-monomethoxy hydroquinone, m-monomethoxy resorcinol, o-monomethoxy catechol, etc. are preferred.

[0040]A compound shown below can be mentioned as an example of a ketone compound expressed with the above-mentioned general formula.

[0041]

[Formula 8]



[0042]As a compound expressed with a general formula (1), 1,2-naphthoquinonediazide 4-sulfonic ester of the aforementioned compound (a), 1,2-naphthoquinonediazide 5-sulfonic ester, 1,2-naphthoquinonediazide 6-sulfonic ester, 1,2-quinone diazide sulfonic ester, such as 2,1-naphthoquinonediazide 4-sulfonic ester, 2,1-naphthoquinonediazide 5-sulfonic ester, and 1,2-benzoquinone diazido 4-sulfonic ester, can be mentioned. Compounds desirable [among these] are 1,2-naphthoquinonediazide 4-sulfonic ester, 1,2-naphthoquinonediazide 5-sulfonic ester, etc.

[0043]The compound expressed with a general formula (1) can be obtained, for example by making a compound (a) and 1 and 2-quinone diazide sulfonyl halide esterify under existence of a basic catalyst. It is desirable especially preferred that 1 per 1 gram equivalent phenolic hydroxyl group of compound (a) and 2-quinone diazide sulfonyl halide is 0.2-1 mol, and the reaction rate of the compound in this case (a) and 1 and 2-quinone diazide sulfonyl halide is 0.4-1 mol.

[0044]An average esterification rate of a compound expressed with a general formula (1) is 30 to 100% preferably. A possibility that definition may fall that an average esterification rate is less than 30%, or pattern shape may worsen is **.

[0045]In addition, 1,2 used by this invention - 1,2-naphthoquinonediazide sulfonic ester can also be used as a naphthoquinonediazide group content compound. As this ester, all or some of hydroxyl group of polyhydric phenol can use a compound esterified with 1,2-naphthoquinonediazide sulfonic acid, 20 to 100% of hydroxyl groups of polyhydric phenol can

use concretely a compound esterified with 1,2-naphthoquinonediazide sulfonic acid. [0046] 1, 2 - as a naphthoquinonediazide group content compound, For example, 2,3,4-trihydroxy benzophenone 1,2 - Naphthoquinonediazide 4- sulfonic ester, 2,3,4-trihydroxy benzophenone 1,2- Naphthoquinonediazide 5- sulfonic ester, 2,4,6-trihydroxy benzophenone 1,2- Naphthoquinonediazide 4- sulfonic ester, 2,4,6-trihydroxy benzophenone 1,2- 1,2-naphthoquinonediazide sulfonic ester of trihydroxy benzophenones, such as naphthoquinonediazide 5- sulfonic ester, 2,2',4,4'-tetrahydroxybenzophenone 1,2- Naphthoquinonediazide 4-sulfonic ester, 2,2',4,4'-tetrahydroxybenzophenone 1,2- Naphthoquinonediazide 5-sulfonic ester, 2,3,4,3'- tetrahydroxybenzophenone 1,2- Naphthoquinonediazide 4-sulfonic ester, 2,3,4,3' - Tetrahydroxybenzophenone 1,2 - Naphthoquinonediazide 5-sulfonic ester, 2,3,4,4'- tetrahydroxybenzophenone 1,2- Naphthoquinonediazide 4-sulfonic ester, 2,3,4,4'- tetrahydroxybenzophenone 1,2- Naphthoquinonediazide 5-sulfonic ester, 2,3,4,2'- Tetrahydroxy-4'-methylbenzophenone 1,2- naphthoquinonediazide 4- sulfonic ester, 2,3,4,2'- tetrahydroxy-4'-methylbenzophenone 1,2- Naphthoquinonediazide 5- sulfonic ester, 2,3,4,4'-tetrahydroxy-3'-methoxybenzophenone 1,2- naphthoquinonediazide 4-sulfonic ester, 2,3,4,4'- tetrahydroxy-3'-methoxybenzophenone 1,2- 1,2-naphthoquinonediazide sulfonic ester of tetrahydroxybenzophenones, such as naphthoquinonediazide 5-sulfonic ester, 2,3,4,2',6'-pentahydroxy benzophenone 1,2- Naphthoquinonediazide 4- sulfonic ester, 2,3,4,2',6'-pentahydroxy benzophenone 1,2- 1,2-naphthoquinonediazide sulfonic ester of pentahydroxy benzophenones, such as naphthoquinonediazide 5- sulfonic ester, 2,4,6,3',4'5'-hexahydroxybenzophenone 1,2- Naphthoquinonediazide 4- sulfonic ester, 2,4,6,3',4' 5'-hexahydroxybenzophenone 1,2- Naphthoquinonediazide 5- sulfonic ester, 3,4,5,3',4' 5'-hexahydroxybenzophenone 1,2- Naphthoquinonediazide 4- sulfonic ester, 3,4,5,3',4' 5'-hexahydroxybenzophenone 1,2- 1,2-naphthoquinonediazide sulfonic ester of hexahydroxybenzophenones, such as naphthoquinonediazide 5- sulfonic ester, Bis(2,4'-dihydroxyphenyl)methane-1,2- Naphthoquinonediazide 4-sulfonic ester, bis(2,4'- dihydroxyphenyl)methane- 1,2 - Naphthoquinonediazide 5-sulfonic ester, Bis(p-hydroxyphenyl)methane-1,2- Naphthoquinonediazide 4- sulfonic ester, Bis(p-hydroxyphenyl)methane-1,2- Naphthoquinonediazide 5- sulfonic ester, Tori (p-hydroxyphenyl) methane-1,2- Naphthoquinonediazide 4- sulfonic ester, Tori (p-hydroxyphenyl) methane-1,2- Naphthoquinonediazide 5- sulfonic ester, 1,1,1-Tori (p-hydroxyphenyl) ethane-1,2- Naphthoquinonediazide 4-sulfonic ester, 1,1,1-Tori (p-hydroxyphenyl) ethane-1,2- Naphthoquinonediazide 5-sulfonic ester, Bis(2,3,4-trihydroxy phenyl)methane-1,2- Naphthoquinonediazide 4- sulfonic ester, Bis(2,3,4-trihydroxy phenyl)methane-1,2- Naphthoquinonediazide 5- sulfonic ester, 2,2-bis(2,3,4-trihydroxy phenyl)propane- 1,2 - Naphthoquinonediazide 4- sulfonic ester. 2,2-bis(2,3,4-trihydroxy phenyl)propane-1,2-

Naphthoquinonediazide 5- sulfonic ester, 1,1,3-tris (2,5-dimethyl- 4-hydroxyphenyl)-3-phenylpropane-1,2- Naphthoquinonediazide 4- sulfonic ester, 1,1,3-tris (2,5-dimethyl- 4-hydroxyphenyl)-3-phenylpropane-1,2- Naphthoquinonediazide 5- sulfonic ester, 4,4'-[1-[4-[1-[methylethyl [4-hydroxyphenyl]-1-]] phenyl] ethylidene] bisphenol 1,2-naphthoquinonediazide 4- sulfonic ester, 4,4'-[1-[4-[1-[methylethyl [4-hydroxyphenyl]-1-]] phenyl] ethylidene] bisphenol 1,2- Naphthoquinonediazide 5- sulfonic ester, Bis(2,5-dimethyl- 4-hydroxyphenyl)-2-hydroxyphenyl methane-1,2- Naphthoquinonediazide 4- sulfonic ester, Screw (2,5-dimethyl- 4-hydroxyphenyl)-2-Hydroxyphenyl methane-1,2-naphthoquinonediazide 5- sulfonic ester, 3,3,3',3'-tetramethyl 1,1'-spiro indene- 5,6,7,5',6',7'-hexanol 1,2-naphthoquinonediazide 4- sulfonic ester, 3,3,3',3'-tetramethyl 1,1'-spiro indene- 5,6,7,5',6',7'-hexanol 1,2-naphthoquinonediazide 5- sulfonic ester, 2,2,4-trimethyl 7,2',4'-trihydroxy flavan 1,2-naphthoquinonediazide 4- sulfonic ester, 2,2,4-trimethyl 7,2',4'-trihydroxy flavan 1,2- 1,2 of alkanes (polyhydroxy phenyl), such as naphthoquinonediazide 5-sulfonic ester - Naphthoquinonediazide sulfonic ester is mentioned.

[0047]These 1, 2 - A naphthoquinonediazide group content compound is independent, or can be combined two or more sorts and can also be used. The above 1,2- naphthoquinonediazide group content compounds are obtained by for example making a halogenide of 1,2-naphthoquinonediazide sulfonic acid esterify with polyhydric phenol (multivalent hydroxy compound) corresponding under existence of a base catalyst. It is desirable to usually use a halogenide of 1,2-naphthoquinonediazide sulfonic acid for such an esterification reaction in quantity of 1.0-1.2 mol to 1 mol of hydroxyl groups of a hydroxy compound.

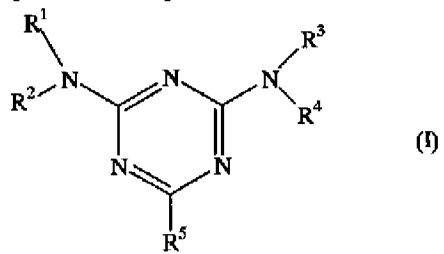
[0048]1, 2 - As for a naphthoquinonediazide group content compound, it is desirable among a photosensitive resin composition concerning this invention that it is usually by 10 - 50 mass-part **** preferably five to 100 mass part to resin (A) 100 mass part. Since there is little acidity generated by exposure when it is less than five mass parts, a solubility difference [as opposed to a developing solution of an exposure part and an unexposed part in a coat formed from this constituent] may become small, and patterning may become difficult, On the other hand, when 100 mass parts are exceeded, by short-time optical exposure, it is 1 and 2. - Since it is not fully decomposed but a naphthoquinonediazide group content compound remains, sensitivity may fall.

[0049]1, 2 which are used for a constituent concerning this invention - As a naphthoquinonediazide group content compound, especially a cyclohexane derivative shown by the above-mentioned general formula (1) is preferred.

[0050][III]If a cross linking agent used for cross linking agent this invention reacts to a functional group in said resin (A) with heating and it has a function which carries out a crosslinking bond, it should not be restricted in particular, but a melamine compound expressed with following formula (I) is mentioned preferably.

[0051]

[Formula 9]



[0052] Formula (I) Naka and R⁵ show -NR⁵¹R⁵² {R⁵¹ and R⁵² shows hydrogen or -CH₂OR⁵³ (R⁵³ shows the alkyl group or cycloalkyl group of hydrogen or the carbon numbers 1-6.) respectively. } or a phenyl group is shown and R¹, R², R³, and R⁴ show hydrogen or -CH₂OR⁵³ (R⁵³ shows the alkyl group or cycloalkyl group of hydrogen or the carbon numbers 1-6.) respectively. As the alkyl group or cycloalkyl group of the above-mentioned R⁵³, a methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl group, an isobutyl group, t-butyl group, n-amyl group, an isoamyl group, n-hexyl group, a cyclohexyl group, etc. are mentioned.

[0053] As an example of a cross linking agent expressed with formula (I) used for this invention, For example, hexamethylolmelamine (R¹, R², R³, R⁴, R⁵¹, and R⁵²) They are -CH₂OH and alkylation hexamethylolmelamine (R¹, R², R³, R⁴, R⁵¹, and R⁵²) respectively. Respectively -CH₂OR⁵³ and R⁵³ preferably The carbon numbers 1-3, Partial methylol-ized melamine (1-5 pieces chosen from R⁵² R¹, R², R³, R⁴, R⁵¹, and -CH₂OH and non selection hydrogen), and its alkylation object (R⁵³ is the carbon numbers 1-3 preferably), Tetramethylol benzoguanamine (R¹, R², R³, and R⁴ are -CH₂OH respectively, and R⁵ is a phenyl group) and alkylation tetramethylol benzoguanamine (R⁵³ is the carbon numbers 1-3 preferably), Partial methylol-ized benzoguanamine (1-3 pieces chosen from R⁴ R¹, R², R³, and -CH₂OH and non selection hydrogen), and its alkylation object (R⁵³ is the carbon numbers 1-3 preferably), Or oligomer (preferably 2-5 monomers) of the above-mentioned compound, etc. can be mentioned.

[0054] As other cross linking agents used by this invention, epoxy compound, a phenol system compound, an azo compound, an isocyanate system compound, etc. are mentioned, and epoxy compound is especially preferred. For example, it is a compound which averages in a molecule and has one or more epoxy groups as an epoxy hardening agent, For example, n-butyl glycidyl ether, 2-ethoxyhexyl glycidyl ether, Phenyl glycidyl ether, allyl glycidyl ether,

ethylene glycol diglycidyl ether, Propylene glycol diglycidyl ether, neopentyl glycol diglycidyl ether, Glycidyl ether, such as glycerol polyglycidyl ether and sorbitol polyglycidyl ether, Glycidyl ester, such as adipic acid diglycidyl ester and o-phthalic acid diglycidyl ester, 3,4-epoxycyclohexylmethyl (3,4-epoxy cyclohexane) carboxylate, 3,4-epoxy-6-methylcyclohexylmethyl (3,4-epoxy-6-methylcyclohexane) carboxylate, Alicyclic epoxy, such as a bis(3,4-epoxy-6-methylcyclohexylmethyl)horse mackerel peat, JISHIKURO pentanediene oxide, and bis(2,3-epoxy cyclopentyl)ether, etc. are mentioned.

[0055]A cross linking agent is 4 - 40 mass part preferably [blending in the range of 2 - 50 mass part to resin (A)], and more preferably. If there are too few loadings, sensitivity may fall, poor development may be caused, and on the other hand, if there are too many loadings, transparency, insulation, and coat nature may worsen.

[0056][IV]In addition, in a positive type photosensitive resin composition of additive agent this invention, a photopolymerization initiator can be contained at everything but the above-mentioned ingredient for promotion of hardening. As a photopolymerization initiator which can be used by this invention, an optical radical polymerization initiator, an optical cationic initiator, an optical amine generating agent, etc. are mentioned.

[0057]As an optical radical polymerization initiator, for example alpha-diketones, such as benzyl and diacetyl. Acyloins, such as benzoin, benzoin methyl ether, benzoin ethyl ether, Acyloin ether, such as benzoin iso-propyl ether, a thioxan ton, Thioxan tons, such as 2,4-diethylthio xanthone and thio xanthone 4-sulfonic acid. Benzophenone, 4,4'-bis(dimethylamino) benzophenone, Benzophenones, such as 4,4'-bis(diethylamino)benzophenone. Michler's ketones, an acetophenone, a 2-(4-toluenesulfonyloxy)-2-phenylacetophenone, p-dimethylamino acetophenone, alpha, and alpha'-dimethoxyacetoxyl benzophenone, A 2,2'-dimethoxy- 2-phenylacetophenone, a p-methoxy acetophenone, 2-methyl[4-(methylthio) phenyl]-2-morpholino 1-propanone, 2-benzyl-2-dimethylamino 1 -(4-morpholinophenyl)-Quinone, such as acetophenones, such as butan-1-one, anthraquinone, and 1,4-naphthoquinone, phenacyl chloride, a trihalomethyl phenylsulfone, Peroxides, such as halogenated compounds, such as tris (trihalomethyl)-s-triazine, acyl phosphine oxide, and di-t-butyl peroxide, etc. are mentioned.

[0058]moreover -- as an optical radical polymerization initiator -- for example, IRGACURE-184 -- said -- 261 -- said -- 369 -- said -- 500 -- said -- 651 -- said -- 907 (made in ****- Guy Gee). Darocur-1173 -- said -- 1116 -- said -- 2959 -- said -- 1664 -- said -- 4043 (made by Merck Japan). KAYACURE-DETX, the said MBP, the DMBI, the EPA, said -- OA (made by Nippon Kayaku Co., Ltd.), and VICURE-10 -- said -- 55 (product made from STAUFFER Co.LTD). TRIGONALP1 (product made from AKZO Co.LTD), and SANDORAY 1000 (product made from SANDOZ Co.LTD), Commercial items, such as DEAP (product made from APJOHN Co.LTD), QUANTACURE-PDO, the said ITX, and the EPD (product made from

WARDBLEKINSOP Co.LTD), can also be used.

[0059]As an optical cationic initiator, diazonium salt, triphenylsulfonium salts, metallocene compounds, diaryl iodonium salts, nitrobenzyl sulfonates, alpha-sulfonyloxy ketone, diphenyldisulfon, and IMIJIRU sulfonates are mentioned. As an optical cationic initiator, ADEKA ultra set PP-33 and OPTMER SP-150, said -- commercial items, such as 170 (diazonium salt (made by Asahi Denka Kogyo K.K.)), OPTOMER SP-150, 170 (made by Asahi Denka Kogyo K.K.) (sulfonium salt), and IRGACURE 261 (made in ****- Guy Gee) (metallocene compound), can also be used.

[0060]As an optical amine generating agent, nitro benzoKABAMI mates and imino sulfonates are mentioned. These photopolymerization initiators are suitably chosen by exposing condition (for example, is it under oxygen environment or is under anoxia atmosphere?) etc., and are used by them. Two or more sorts of these photopolymerization initiators can be combined, and they can also be used.

[0061]A photopolymerization initiator is more preferably blended in quantity of zero to 2 mass part zero to 5 mass part to solid content 100 mass part of a photosensitive resin composition of this invention. When quantity of a photopolymerization initiator exceeds five mass parts, a photopolymerization initiator may carry out bleed out from a paint film surface formed from a photosensitive resin composition of this invention, or heat-treatment may fall.

[0062]A positive type photosensitive resin composition of this invention can be used for a means to adjust the physical properties of a positive image, by being able to include a photopolymerization nature monomer and selecting this quantity and kind. A photopolymerization nature monomer is an ingredient which polymerizes by exposure. Specifically, monofunctional nature, polyfunctional methacrylate, or acrylate (it is hereafter described as acrylate (meta).) is mentioned preferably. A photopolymerization nature monomer may contain fluoride.

[0063]As monofunctional nature (meta) acrylate, for example ARONIKKUSU M-101, said M-111, said M-114 (product made from Toagosei Chemical industry), KAYARADTC-110S, the TC-120S (made by Nippon Kayaku Co., Ltd.), V-158, V-2311 (made by OSAKA ORGANIC CHEMICAL INDUSTRY, LTD.) (commercial item), etc. are mentioned.

[0064]As 2 functionality (meta) acrylate, for example ARONIKKUSU M-210, said M-240, said M-6200 (product made from Toagosei Chemical industry), KAYARADDDDA, the HX-220, said R-604 (made by Nippon Kayaku Co., Ltd.), V260, V312, V335H.P. (made by OSAKA ORGANIC CHEMICAL INDUSTRY, LTD.) (commercial item), etc. are mentioned.

[0065]As acrylate (meta) of three or more functionality, For example, TORIMECHI roll pro pantry (meta) acrylate, penta ERIS RITORUTORI (meta) acrylate, Tris acryloyloxyethyl phosphate, pentaerythritol tetra (meta) acrylate, Dipentaerythritol penta (meta) acrylate, dipentaerythritol hexa (meta) acrylate, etc. are mentioned, Concretely ARONIKKUSU M-309,

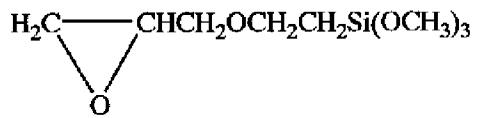
said M-400, said M-405, said M-450, said M-7100, said M-8030, said M-8060 (product made from Toagosei Chemical industry), KAYARAD DPHA, the TMPTA, the DPCA-20, said-30, said-60, said-120 (made by Nippon Kayaku Co., Ltd.), Commercial items, such as V-295, said-300, said-360, the -GPT, the -3PA, said-400 (made by OSAKA ORGANIC CHEMICAL INDUSTRY, LTD.), and PPZ (product made from Idemitsu Petrochemistry), are mentioned.

[0066] Polyfunctional (meta) acrylate of three or more functionality, such as ARONIKKUSU M-400 and KAYARAD DPHA, is used preferably among these. Two or more sorts of these monomers can be combined, and they can also be used.

[0067] 0-3 mass-part combination of the photopolymerization nature monomer is more preferably carried out zero to 10 mass part to alkalis-soluble-resin (A)100 mass part. The photosensitive resin composition concerning this invention can raise adhesion with a substrate by including a silane coupling agent. As a silane coupling agent, a functionality silane coupling agent etc. are mentioned preferably. As a functionality silane coupling agent, although the following are illustrated, S3 and S4 are especially preferred.

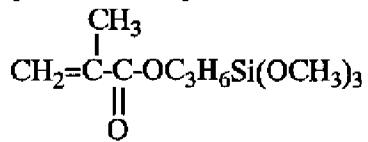
S1. vinyltriethoxysilane : $\text{CH}_2=\text{CHSi(OCH}_2\text{H}_4\text{OCH}_3)_3$ S2. vinyltris (beta-methoxyethoxy) Silang: $(\text{OC}_2\text{H}_5)_3\text{CH}_2=\text{CHSi(OCH}_2\text{H}_4\text{OCH}_3)_3$ S3. gamma-glycidoxypropyltrimetoxysilane : [0068]

[Formula 10]



[0069] S4. gamma-meta-acryloxypropyltrimethoxysilane : [0070]

[Formula 11]



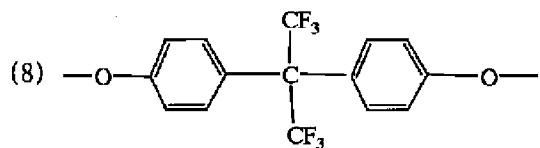
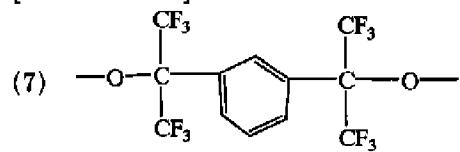
[0071] S5. gamma-mercaptopropyltrimethoxysilane: -- a $\text{HSC}_3\text{H}_6\text{Si(OCH}_3)_3$ silane coupling agent receives alkalis soluble resin (A) -- ***** for 0.01 - 5 mass parts -- things are preferred. Two or more sorts of these can also be used. Such a silane coupling agent may be preferably contained in the quantity of one or less mass part two or less mass parts, when making the whole quantity in a photosensitive resin composition into 100 mass parts.

[0072] The photosensitive resin composition of this invention so that a fluorine atom may contain in the hardening layer, The pattern state thin film which was excellent in low dielectric property in addition to other various characteristics can be preferably formed more easily into the solid content of the photosensitive resin composition of this invention by 5-30 mass % content making [more than 3 mass %] a fluorine atom more desirable. A fluorine compound is

used as a source of a fluorine atom which can give the pattern state thin film which was excellent in such low dielectric property. The fluorine compound used in this invention may be combined with the carboxyl group contained in resin (A) at the time of sensitization and heating, and, Or it may be combined with a cross linking agent and may polymerize in fluorine compounds further, and it may exist as a mixture of a photosensitive resin composition, without reacting to these. The typical example of a fluorine compound is the compound which the fluorine-containing basis shown in following the (1) - (8) combined.

[0073](1) F. $(CF_2)_n$. (2) $(CF_3)_2CF(CF_2)_{n-2}$ - [(3) $H(CF_2)_n$] (4) CF_3CHFCF_2 - (5) $(CF_3)_2CH$ - (6) $-(CF_2CCIF)-$ [0074]

[Formula 12]



[0075]here -- n -- usually -- 1-10 -- it is 5-8 preferably. In a formula (7) and (8), hydrogen of the benzene ring may be replaced by fluoride and other substituents, and the benzene ring may be alicyclic-ized.

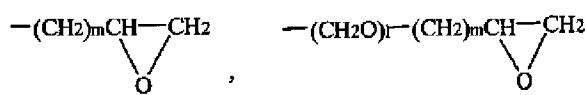
[0076]As a fluorine compound, alcohols, carboxylic acid, epoxy compounds, olefins, a halogenation compound, acrylate, methacrylate, ester species, ether, amines, etc. can be mentioned. Especially, epoxy compounds, acrylate, methacrylate, and amines are preferred.

[0077]The compound which the fluorine-containing basis shown in the basis shown in the following table 1 and above-mentioned (1) - (8) as an example of the epoxy compounds containing these fluorine atoms, acrylate, methacrylate, and amines combined can be mentioned.

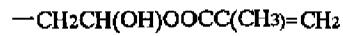
[0078]

[Table 1]

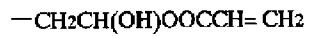
エポキシ化合物類

 $m=1-3, l=1-3$

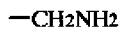
メタクリレート類



アクリレート類

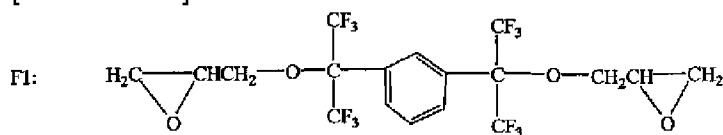


アミン類



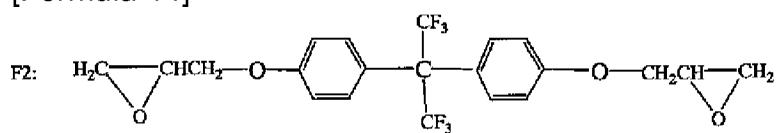
[0079] Although a basis which contains epoxy, for example as epoxy compounds in a frame of the above-mentioned table 1 is indicated, the epoxy compounds mean various epoxy compounds which a fluorine-containing basis etc. which are indicated to basis and above (1) - (8) join together, and are formed. The same may be said of other compounds. As a fluorine compound, epoxy compounds and amines are especially preferred, and a fluoridation aliphatic compound with a fluorine-containing basis of aliphatic series, such as a fluoridation aromatic epoxy compound and the above (1), with a fluorine-containing basis of aromatic systems, such as the above (7) and (8), is especially preferred. As the desirable example of a fluoridation aromatic epoxy compound, [0080]

[Formula 13]



[0081] 2,2'-[bis[1,3-phenylene] [[2,2,2-trifluoro-1-(trifluoromethyl) ethylidene] oxymethylene]] bis-oxirane[0082]

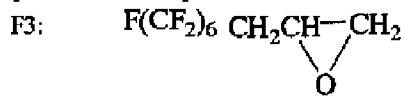
[Formula 14]



[0083]2,2-bis[4-(2,3-epoxy propoxy) phenyl] hexafluoropropane is mentioned, and the following compound is mentioned as a desirable example of a fluoridation aliphatic compound.

[0084]

[Formula 15]



[0085]The photosensitive resin compositions of this invention are resin (A), and 1 and 2. - If needed, a photopolymerization initiator, a silane coupling agent, a fluorine compound, etc. are dissolved in a solvent, and it is prepared by a naphthoquinonediazide group content compound and a cross linking agent, and others.

[0086]As a solvent for dissolving the photosensitive resin composition of this invention, Ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, Ethylene glycol monopropyl ether, ethylene glycol monobutyl ether, Ethyleneglycol dimethyl ether, ethylene glycol diethylether, Ethylene glycol dipropyl ether, propylene glycol monomethyl ether, Propylene glycol monoethyl ether, propylene glycol monopropyl ether, Propylene glycol monobutyl ether, propylene glycol wood ether, Propylene glycol diethylether, diethylene glycol monomethyl ether, Diethylene glycol monoethyl ether, diethylene-glycol monophenyl ether, Diethylene glycol dimethyl ether, diethylene-glycol diethylether, Ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, ethylene glycol monopropyl ether acetate, ethylene-glycol-monobutyl-ether acetate, ethylene-glycol-monophenyl-ether acetate, Diethylene-glycol-monomethyl-ether acetate, diethylene glycol monoethyl ether acetate, Diethylene-glycol monopropyl ether acetate, diethylene glycol monobutyl ether acetate, Diethylene-glycol monophenyl ether acetate, propylene-glycol-monomethyl-ether acetate, Propylene glycol monoethyl ether acetate, propylene glycol monopropylether acetate, 2-methoxy butyl acetate, 3-methoxy butyl acetate, 4-methoxy butyl acetate, 2-methyl-3-methoxy butyl acetate, 3-methyl-3-methoxy butyl acetate, 3-ethyl-3-methoxy butyl acetate, 2-ethoxybutyl acetate, 4-ethoxybutyl acetate, 4-propoxybutyl acetate, 2-methoxy pentyl acetate, 3-methoxy pentyl acetate, 4-methoxy pentyl acetate, 2-methyl-3-methoxy pentyl acetate, 3-methyl-3-methoxy pentyl acetate, 3-methyl-4-methoxy pentyl acetate, 4-methyl-4-methoxy pentyl acetate, acetone, Methyl ethyl ketone, a diethyl ketone, methyl SHISOBUCHIRU ketone, ethyl isobutyl ketone, A tetrahydrofuran, cyclohexanone, methyl propionate, ethyl propionate, Propionic acid propyl, propionic acid isopropyl, 2-methyl hydroxypropionate, 2-

ethyl hydroxypropionate, 2-hydroxy-2-methyl, Methyl-3-methoxy propionate, ethyl-3-methoxy propionate, Ethyl-3-ethoxy propionate, ethyl-3-propoxy propionate, Propyl-3-methoxy propionate, isopropyl-3-methoxy propionate, 2-hydroxy-ethoxyethyl acetate, oxyethyl acetate, and methyl 3-methylbutanoate, Methyl acetate, ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate, Isoamyl acetate, methyl carbonate, ethyl carbonate, propyl carbonate, butyl carbonate, Methyl pyruvate, ethyl pyruvate, pyruvic acid propyl, pyruvic acid butyl, methyl acetoacetate, ethyl acetoacetate, benzylmethyl ether, benzyl ethyl ether, dihexyl ether, benzyl acetate, ethyl benzoate, a diethyl oxalate, a diethyl maleate, Gamma-butyrolactone, benzene, toluene, xylene, cyclohexanone, methanol, ethanol, propanol, butanol, a hexanol, cyclohexanol, ethylene glycol, a diethylene glycol, glycerin, etc. can be mentioned.

[0087]In this invention, in order to raise improvement in the spreading nature of a photosensitive resin composition, for example, prevention of striae SHON (after spreading ****), and the development nature of a coat, a surface-active agent can also be blended. As a surface-active agent, for example Polyoxyethylene lauryl ether, Polyoxyethylene alkyl ether, such as polyoxyethylene stearylether and polyoxyethylene oleylether. Polyoxyethylene aryl ether, such as polyoxyethylene octylphenyl ether and polyoxyethylene nonylphenyl ether, The Nonion system surface-active agents, such as polyoxyethylene dialkyl ester, such as a polyoxyethylene JIRAU rate and polyoxyethylene distearate, EFUTOPPUEF301 -- said -- 303 -- said -- 352 (made in new Akita Chemicals). The megger fuck F171, said F172, said F173, said F177 (made by Dainippon Ink & Chemicals, Inc.), Fluorad FC-430, the FC-431 (made by Sumitomo 3M), A fluorochemical surfactant marketed under the name of Asahi guard AG710, the Sir chlorofluocarbon S-382, the SC-101, the SC-102, the SC-103, the SC-104, the SC-105, the SC-106 (made by Asahi Glass Co., Ltd.), etc., Organosiloxane polymer KP341 (made by Shin-Etsu Chemical Co., Ltd.), acrylic acid series (meta) copolymer poly flow No. 57, 95 (product made from Kyoeisha Fatty chemistry Industry) etc. is mentioned.

[0088]Two or more sorts of these can also be used. Such a surface-active agent may be preferably contained in quantity of one or less mass part two or less mass parts, when making the whole quantity in a photosensitive resin composition into 100 mass parts.

[0089]In order to raise the heat resistance of a photosensitive resin composition, and adhesion with a substrate, a compound which has at least two epoxy groups may be included in intramolecular. as such an epoxy group containing compound -- Epicoat 1001 -- said -- 1002 -- said -- 1003 -- said -- 1004 -- said -- 1007 -- said -- 1009 -- said -- 1010 -- said -- bisphenol A type epoxy resins, such as 828 (trade name; product made from Oil recovery Shell Epoxy),. Bisphenol F type epoxy resin, such as Epicoat 807 (trade name; made by a Japan epoxy resin company), Epicoat 152 -- said -- 154 (trade name; made by a Japan epoxy resin company). EPPN201 -- said -- phenol novolak type epoxy resin, such as 202 (trade name; made by Nippon Kayaku Co., Ltd.),. EOCN102, said 103S, said 104S, 1020, 1025, 1027 (trade name;

made by Nippon Kayaku Co., Ltd.), Cresol novolak type epoxy resin, such as Epicoat 180S75 (trade name; made by a Japan epoxy resin company), CY-175 -- said -- 177 -- said -- 179 and Arda light CY-182 -- said -- 192 and 184 (trade name; made in ****- Guy Gee). ERL-4234, 4299, 4221 and 4206 (trade name; made by a U.C.C company), show dyne 509 (trade name; made by Showa Denko K.K.), and Epiclon 200 -- said -- 400 (trade name; made by Dainippon Ink), and Epicoat 871. said -- 872 (trade name; made by a Japan epoxy resin company), and ED-5661 -- said -- annular aliphatic series epoxy resins, such as 5662 (trade name; product made from Cera Needs Coating),. Aliphatic series poly glycidyl ether, such as EPO light 100MF (product made from Kyoeisha Fatty chemistry Industry) and EPIORU TMP (made by Nippon Oil & Fats Co., Ltd.), etc. are mentioned.

[0090]Also among these, a bisphenol A type epoxy resin, bisphenol F type epoxy resin, phenol novolak type epoxy resin, cresol novolak type epoxy resin, aliphatic series poly glycidyl ether, etc. are used preferably.

[0091]A molecular weight in particular of the above epoxy group containing compounds may not be limited, and may be the amount of polymers, and may be low molecular weight, such as glycidyl ether of bisphenol A (or F).

[0092]An epoxy group containing compound as an optional component is used to resin (A) 100 mass part if needed in quantity of 5 - 50 mass part. In a photosensitive resin composition of this invention, a spray for preventing static electricity, preservation stabilizer, an antihalation agent, a defoaming agent, paints, etc. can also be added if needed.

[0093]By using a photosensitive resin composition of this invention, a pattern can be formed as follows, for example. First, each ingredient is dissolved in a solvent so that concentration of the solid content may become 5 - 60 mass %, for example, and a photosensitive resin composition solution of this invention is prepared by filtering this with a filter with an aperture of about 0.2-10 micrometers. And a photosensitive resin composition solution of this this invention is applied to the surface of substrates, such as a silicon wafer, by prebaking, a solvent is removed and a coat of a photosensitive resin composition is formed. Subsequently, after performing radiation irradiation treatment (the 1st exposure), such as optical irradiation treatment, to a formed coat, a positive pattern is formed by performing a development and removing a radiation irradiation portion. In order [which may be sake / in order / and also exposed (the 2nd exposure) and heightens an effect of exposure further] to raise various characteristics, such as the solvent resistance of a pattern obtained by development, film strength, and heat resistance, a pattern may be heated either under [before exposure] exposure or after exposure. As for this heat-treatment, being given after exposure is preferred preferably, and it is preferred that light volume of the 2nd exposure is 2 to 15 times that of the 1st exposure. It is preferred for the 2nd light exposure to make a light exposure of the 1st exposure 20 - 150 mJ/cm², and to consider it as the two to 15 times in a method of this

invention. As for heat-treatment, 100-220 ** and 3 to 60 minutes are preferred.

[0094]As a method of applying a photosensitive resin composition solution of this invention to a substrate, various kinds of methods, such as a spin coating method, a flow-coating cloth method, and a roll coating method, are employable. Cooking temperature is 50-150 **, and cooking time of conditions of prebaking is for [for / 30 seconds / -] 600 seconds, for example. As radiation used for radiation irradiation treatment, By ultraviolet rays from an ultra-high pressure mercury lamp etc., i line with a wavelength of 365 nm, h line with a wavelength of 405 nm, Charged particle beams, such as X-rays, such as far ultraviolet rays, such as a with a g line of 436 nm, a KrF excimer laser with a wavelength of 248 nm, and a wavelength of 193 nm ArF excimer laser, and a synchrotron radiation line, or an electron beam, are mentioned.

[0095]As a developing solution used for a development, preferably, For example, sodium hydroxide, sodium carbonate, silic acid sodium, meta-silic acid sodium, An ammonia solution, ethylamine, n-propylamine, diethylamine, Di-n-propylamine, triethylamine, methyldi ethylamine, dimethylethanolamine, triethanolamine, tetramethylammonium hydroxide, tetraethylammoniumhydroxide, Kolin, pyrrole, piperidine, 1, 8-diazabicyclo [5.4.0]-7-undecene, 1, 5-diazabicyclo [4.3.0]An alkaline aqueous solution in which it comes to dissolve-5-nonane etc. is mentioned. A thing which comes to add a proper quantity of alcohols, such as a water soluble organic solvent, for example, methanol, and ethanol, and surface-active agents can also be used for this alkaline aqueous solution. Development time is, for example for 10 to 300 seconds, and can use a liquid peak method, a dipping method, rocking dip coating, etc. as a developing method. After alkaline development, although rinsing treatment by stream washing is performed, as rinsing treatment, rinsing by ultra-high pressure Microjet is preferred.

[0096]As for ultra-high pressure Microjet, water is injected from a high-pressure-jet device.

impressed pressure of ultra-high pressure Microjet -- usually -- 20 - 350 kgf/cm² (2.9 - 34.3MPa) -- a thing of 30 - 250 kgf/cm² (4.9 - 24.5MPa) is pointed out preferably. This impressed pressure is selected by shape of a nozzle and its cat form nozzle (a section is the shape of a concave lens) is preferred in this invention. Angles of spray of ultra-high pressure Microjet have big influence on a rinsing operation. A rinsing operation has the strongest case of being vertical, to a field of a photosensitive resin composition. As for removal of a constituent of a non-exposing part, on the other hand, it is [a rinsing operation] insufficient that it is just strong, If a shock of mechanical water does not remove an unnecessary constituent from a substrate, there is nothing, but for that purpose, to a substrate, although a jet direction is perpendicularly the best, an angle of the perpendicular direction and a jet direction to a substrate to make may inject it to before or back to a direction of movement of a substrate as about **0 to 20 degrees.

[0097]Although it is practical to adopt continuation rinsing as an economical embodiment of this invention, In that case, so that water may spread crosswise [of a photosensitive resin

composition layer] uniformly, It is preferred independent or to take a method of passing an injection portion of water while carrying out multiple arrays in the spread direction of a fan and carrying out constant-speed movement of the photosensitive resin composition to the direction of injection of the shape of the fan in rectangular directions, and to perform continuation rinsing treatment for an injection nozzle injected with a spread of fanning.

[0098]Since the depths of a non-exposed area layer are also removed effectively, it is also possible to use it also for a big constituent of thickness which is generally hard to remove, and a good pattern of a profile can be made to form in this method.

[0099]Especially as for a high-pressure-jet device which has a function for filling the above-mentioned injection pressure, the angle of impact, stream spread shape, etc., and can be used preferably, ultra-high pressure jet precision cleaning system AF series (Asahi Sunac Corp.) is mentioned. Especially, relatively, AF5400S is suitable for high voltage injection, and AF2800II is relatively suitable for low pressure injection. However, if it is a device which has above-mentioned injection applied pressure, the angle of impact, stream spread shape, etc., it is not limited to this model but can apply to a rinsing means after development in a pattern formation method of this invention.

[0100]In this method, an effect of ultra-high pressure Microjet is powerful, and since the depths are attained to, a non-pattern part is substantially removed by rinsing by water.

[0101]A pattern state thin film which a resin composition currently patternized performed air-drying, said 2nd exposure, and heat-treatment by after the above-mentioned rinsing treatment (for example, compressed air and compressed nitrogen), and was hardened is formed on a substrate. In this way, a pattern state thin film obtained is excellent in physical properties, such as high resolution, surface smoothness, high resolution nature, development nature, heat resistance, chemical resistance, adhesion with a substrate, transparency, and insulation. In addition to the above-mentioned characteristic, in a photosensitive resin composition, the specific inductive capacity is 3 or less, and desirable 2.8 or less and a low thing what contains a fluorine compound further. Therefore, a photosensitive resin composition of this invention is useful to a protective film of electronic parts, a flattening film, an interlayer insulation film, etc., and especially useful to micro lenses, such as an interlayer insulation film of a liquid crystal display element, an integrated circuit device, and a solid state image pickup device, and a solid state image pickup device.

[0102]

[Example]Hereafter, although the photosensitive resin composition of this invention is explained based on an example, this invention is not limited to these.

[0103]3 yuan copolymer (copolymerization ratio 70:20:10; average molecular weight 15,000 [about]) 60 mass part which consists of example 1N-(4-hydroxyphenyl) maleimide, styrene, and t-butyl methacrylate, The sensitizing agent a-1 (2S: two of three hydroxyl groups replace)

15 above-mentioned mass part of this invention, hexamethoxy methylolmelamine 22 mass part, and propylene-glycol-monomethyl-ether acetate 200 mass part were mixed, the stirring dissolution was carried out, and the photosensitive resin composition was prepared.

[0104]On a glass substrate (Corning 7059), after thickness carries out spin spreading so that it may be set to 3 micrometers, this on a hot plate, Make it dry for 2 minutes and it lets 100 ** of masks of the pattern of a 4-micrometer angle pass, It exposed with the light exposure of 100 mJ/cm^2 using the ultrahigh pressure mercury lamp, and with the developing solution made from Fuji Photo Film Arch, and the developing solution which diluted trade name CD2000 to two thirds, negatives were developed for 60 seconds, it rinsed and dried at 25 **, and the minute pattern was obtained. Then, the whole substrate is exposed the 2nd time with the light exposure of 200 mJ/cm^2 , and it heat-treated for 2 minutes and was made to harden at 200 **.

[0105]The following method estimated the characteristic of the obtained pattern state heat cure film.

[0106](1) Measurement of specific inductive capacity : the specific inductive capacity of the heat cure film obtained above was measured using the dielectric constant measuring device (made by Hewlett Packard) on a room temperature and 1-MHz conditions. Specific inductive capacity was 3.1.

[0107](2) After measuring the thickness of the heat-resistant heat cure film of the evaluation above, it heated for 60 minutes within 220 ** oven. And the thickness after heat-treatment was measured. There was almost no change of the thickness by heating.

[0108](3) The heat cure film of the evaluation above of solvent resistance was immersed in the NMP (N-methyl-2-pyrrolidone) solution for 10 minutes at the room temperature, and the thickness after rinsing and desiccation was measured. There was almost no thickness change by immersion.

[0109](4) The heat cure film of the evaluation above of exfoliation tolerance was immersed in the mixed liquor (8:2) of 80 ** dimethyl sulfoxide and diethanolamine for 15 minutes, and it rinsed and dried. There was also no exfoliation of a film and there was also no thickness change.

[0110](5) The heat cure film of the measurement above of transparency was measured on 380 to 700 nm wavelength using the double beam type spectrophotometer, and it asked for transmissivity. The film was transparent, there was almost no absorption of long wavelength, and the transmissivity of 400 nm was also 95% also in short wavelength.

[0111](6) It had hardened, with rectangular shape maintained, without becoming the shape having carried out the heat flow and roundish also with heating, as a result of a scanning electron microscope's (SEM's) estimating a section for the heat cure film of the evaluation above of pattern shape.

[0112]In comparative example 1 Example 1, instead of N-(4-hydroxyphenyl) maleimide which

is a copolymer component of this invention, The copolymer (copolymerization ratio 70:20:10; average-molecular-weight about 15,000) produced using hydroxystyrene was used, and also the photosensitive resin composition was prepared like Example 1. Although it let the mask pass like Example 1 and exposure and development were performed about the obtained resin composition, probably because the solubility to an alkali developing solution was high, the remaining rate of membrane was low, the thickness of the pattern was thin, and a good pattern was not obtained. Due to the heat-treatment (200 **, 2 minutes) after the 2nd exposure, the rectangular shape after development carried out the heat flow, and collapsed, and it became the shape in which line width spreads and which is roundish. That is, compared with resin of this invention of Example 1, it is easy to carry out heat modification of the resin used by the comparative example 1.

[0113]In example 2 Example 1, a-1 used as a sensitizing agent was changed into a-9, and also the photosensitive resin composition was prepared like Example 1.

[0114]In example 3 Example 1, a-1 used as a sensitizing agent was changed into a-17, and also the photosensitive resin composition was prepared like Example 1.

[0115]In example 4 Example 1, a-1 used as a sensitizing agent was changed into a-18, and also the photosensitive resin composition was prepared like Example 1.

[0116]In example 5 Example 1, a-1 used as a sensitizing agent was changed into a-8, and also the photosensitive resin composition was prepared like Example 1.

[0117]In example 6 Example 1, changed into 4,4'-[1-[4-[1-[methyl]ethyl [4-hydroxyphenyl]-1-] phenyl] ethylidene] bisphenol 1,2-naphthoquinonediazide 4- sulfonic ester a-1 used as a sensitizing agent, and also. The photosensitive resin composition was prepared like Example 1.

[0118]When the described method estimated the characteristic of the pattern state heat cure film produced by processing the photosensitive resin composition of the above-mentioned Examples 2-6 like Example 1, it was the same as that of Example 1 almost about specific inductive capacity, heat resistance, solvent resistance, transparency, and thermochromism. Although the radius of circle came only out of Example 6 a little with heating after the 2nd exposure and shape changed about pattern shape, it was a satisfactory level practical. About other Examples 2-5, pattern shape hardly changed like Example 1.

[0119]N-(4-hydroxyphenyl) maleimide used in comparative example 2 Example 1, Except having used the copolymer (average-molecular-weight about 15,000) which changed into 45:30:25 the copolymerization ratio of a 3 yuan copolymer which consists of styrene and t-butyl methacrylate, the photosensitive resin composition was prepared like Example 1, and it was similarly estimated as Example 1. Compared with Example 1, a development remaining rate of membrane is low, a pattern chips and pattern formation nature is inferior.

[0120]

[Effect of the Invention] The photosensitive resin composition of this invention can be developed with an alkaline aqueous solution, and are high resolution and high sensitivity. And realizing conventionally simultaneously with the characteristic of these with various characteristics, such as heat resistance, solvent resistance, exfoliation tolerance, and transparency, can form easily the pattern state thin film which was excellent in the difficult low dielectric property.

Therefore, the photosensitive resin composition of this invention as a positive resist for creating the mask for circuit manufacture of an integrated circuit, the thin film for liquid crystal displays, a transistor circuit, etc., Furthermore, it can be conveniently used also as permanent film formation materials, such as an interlayer insulation film, a protective film for light filters, and a micro lens.

[Translation done.]